

# Properties of Fast-Decay Cathode-Ray Tube Phosphors

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*Cathodoluminescent efficiency, decay time, aging characteristics, spectral distribution, and temperature dependence of luminescent emission have been measured for the more intense fast-decay phosphors. Materials studied were  $\text{ZnS}(\text{Ag}, \text{Ni})$ ;  $\text{ZnO}(\text{Zn}) = \text{P24}$ ;  $\text{BaPbSO}_4$ ;  $(\text{CaO})_2 \cdot \text{MgO} \cdot (\text{SiO}_2)_2 \cdot (\text{Ce}) = \text{P16}$ ; and  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_2 \cdot (\text{Ce}) = \text{P16}$ .*

*The intensities of the P16 and P24 samples were observed, to a good approximation, to be proportional to the decay times. Aging due to electron bombardment was found to be fastest for  $\text{BaPbSO}_4$  and the P16 CaMg-silicate, slower for the P16 CaAl-silicate, and slowest for P24 and  $\text{ZnS}(\text{Ag}, \text{Ni})$ . The decay was nonexponential for all the phosphors studied and the decay time became shorter with increasing beam current density. The intensity generally decreased with temperature, reaching 10 per cent of the room temperature value at about 200°C, 300°C, 350°C, 600°C, for the  $\text{ZnS}(\text{Ag}, \text{Ni})$ ,  $\text{BaPbSO}_4$ , P24, and CaAl-silicate, respectively. The CaMg-silicate retains 90 per cent of its 20°C intensity at a temperature of 600°C.*

*Investigations were also conducted on optimum screen weight, effects of particle size distribution, and on screen preparation techniques, all of which will be discussed.*

*It is concluded that phosphor characteristics differ significantly between batches and manufacturers. A detailed evaluation of the important parameters should be conducted on individual phosphor batches for applications where screen characteristics are critical.*

## 1. INTRODUCTION

When selecting a phosphor for cathode-ray tube applications, it is important to consider the efficiency, decay time, aging characteristics, spectral distribution, and temperature dependence of the luminescent emission. The present paper describes the results of measurements of these characteristics on numerous samples of fast-decay ( $\tau \lesssim 1 \mu\text{sec}$ )

phosphors of the  $\text{ZnS}(\text{Ag}, \text{Ni})$ ,  $\text{ZnO}(\text{Zn})$ ,  $\text{BaPbSO}_4$ ,  $(\text{CaO})_2 \cdot \text{MgO} \cdot (\text{SiO}_2)_2$ , and  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_2$  types. The first section deals with experimental procedures used in the determination of the phosphor characteristics. The succeeding sections discuss the specific characteristics of the phosphors studied.

The work described in this paper was undertaken in connection with the selection of a phosphor for the screen of the cathode-ray tube of the flying spot store, a semipermanent memory developed for use in an experimental electronic telephone switching system.

## II. EXPERIMENTAL PROCEDURES

Many luminescent properties of phosphors depend strongly on the mode of excitation because of their dependence on parameters such as the absorption coefficient of the exciting radiation, excitation density, temperature effects, etc. Phosphor evaluation experiments should utilize excitation conditions as similar as possible to those to be used in the application. If exact duplication is not attained, it is necessary to determine the limits of the validity of the tests.

### 2.1 Screen Preparation

All commercial samples measured were used as received, without any grinding or other mechanical processing prior to the settling operation. During screen settling, the required phosphor quantity is suspended by ultrasonic agitation in a solution of potassium silicate (density  $1.07 \text{ g/cm}^3$ ). This suspension is poured into an aqueous solution of barium nitrate ( $22.5 \text{ g/l H}_2\text{O}$ ) which covers the surface to be coated. The settling time depends on the density of the phosphor and varies between one and several hours. The composition of the settling solution is critical if optimum screen adherence is to be achieved.<sup>1</sup> Care must be taken to use purified chemicals and water; otherwise screen adherence may be poor, or the phosphor may be poisoned by the diffusion of impurities during tube baking.

Screen settling with potassium silicate,  $\text{K}_2\text{SiO}_3$ , is based on the adsorption of silica acid ions ( $\text{SiO}_2^-$ ) on the surface of the particles and the glass. These strong negative charges create a repulsive force which prevents coagulation and adherence of the particles. The addition of a salt, for example  $\text{Ba}(\text{NO}_3)_2$ , decreases the negative potential and enhances the formation of oxygen bridges between the silica acid ions. This leads to gelatination and strong adhesion between the particles as well as between the particles and the glass.<sup>2,3,4</sup>

For aging measurements, the screens were backed with a layer of aluminum 500–600 Å thick. This layer acts as an ion trap and also reflects that part of the fluorescent light which would otherwise be lost in the interior of the tube.<sup>5</sup> It was found that the thickness of the aluminum layer must be greater than 300 Å for maximum reflection, in agreement with measurements published in the literature.<sup>5, 6</sup>

## 2.2 *Measurement of Relative Intensity and Decay Time*

The relative intensity and the absolute value of the decay time ( $1/e$  point) were measured with a continuously pumped demountable tube. This does not approach the environment of a sealed-off tube very closely, as the pressure in the system was relatively high ( $8$  to  $12 \times 10^{-6}$  mm Hg). The screens were not aluminized and no processing (heat treatment) of the tube was done. Some comparative experiments indicated, however, that the results were proportional to the values obtained in sealed-off tubes.

In agreement with the observation of other authors,<sup>7,8</sup> it was found that the use of oil pumps reduces the secondary emission ratio of the screens, leading to a rapid decrease of the phosphor surface potential and consequently the emission intensity. This effect persisted when a liquid nitrogen cold trap was added to the system, but was eliminated when the oil diffusion pump was replaced by a mercury type.

The phosphors were settled on microscope slides. Up to 6 samples could be introduced simultaneously into the tube and tested under identical conditions. The grid of the electron gun (5W/5Z type) was pulsed 1000 times per second with pulses of 5  $\mu$ sec length; the beam voltage was 10 kv and the current density in the focussed beam about 5 ma/cm<sup>2</sup>. The output light pulse was observed with a photomultiplier having an S11 spectral response and displayed on the screen of an oscilloscope. It was possible to expand the display of the decay and to read the decay time with high precision directly on the vernier of a variable delay (Fig. 1). This method has also been used to determine the form of the decay. The shortest decay time which could be measured was of the order of 50 nsec.

Relative intensities were measured using a P16 reference phosphor as a standard. The reference slide was changed sufficiently often so that deterioration by electron and ion bombardment remained negligible during the time necessary for the measurements.

Measurements of the fluorescent intensity in the demountable station were only possible in relative units. To determine the absolute values

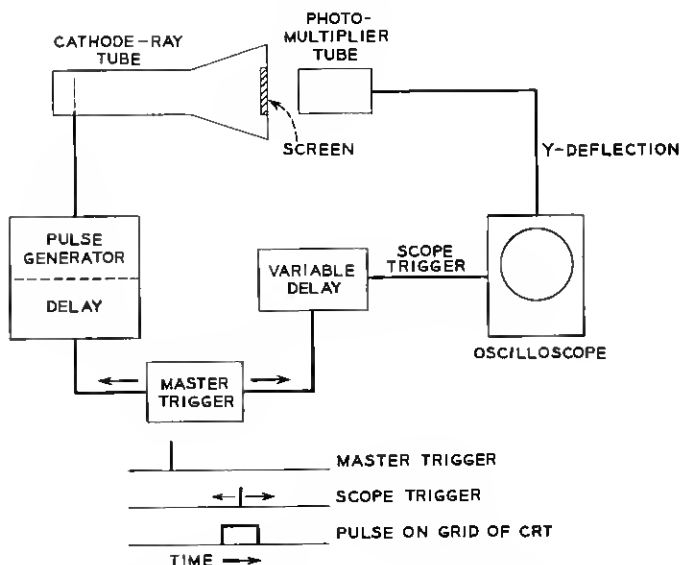


Fig. 1 — Schematic of the circuit for measuring decay times of fast-decay cathode-ray tube phosphors.

of the energy conversion efficiency under operating conditions a few small sealed-off cathode-ray tubes were made with screens from three different phosphor samples. The emission intensity from these tubes operating under standard excitation conditions was then compared with a calibrated light source<sup>9,10</sup> consisting of a P16 phosphor excited by the long-life radioactive isotope  $\text{Sr}^{90}$ . For technical reasons a light flux of  $1.1 \times 10^{-3}$  watts from a phosphor screen with P16 spectral distribution was called one "R." For green light as emitted by a P24 phosphor the corresponding figure is  $1.5 \times 10^{-3}$  watts.

### 2.3 Measurement of the Aging Characteristics

The decrease of the luminescent efficiency of the screen with life in cathode-ray tubes is dependent on the total (time-integrated) deposited electron charge per unit area of the screen and the bombardment by negative ions produced by electron ionization of the residual gas also contribute.

To minimize ion effects, as well as contaminating deposits from pump fluid vapors and rubber gasket joints which are unavoidable in demountable stations, it was necessary to study the aging characteristics under

clean vacuum conditions. All aging data presented here were therefore obtained with sealed-off tubes using aluminized screens. The processing of the testers consisted of baking for three hours at 380°C, R<sub>1</sub> outgassing of the metal parts, and flashing the getters. The seal-off pressure was about 10<sup>-7</sup> mm Hg.

All tubes were aged with direct current at 10 kv. The aged spots ranged in area from 15–25 mm<sup>2</sup>. A power density of 0.6 watt/cm<sup>2</sup> was found small enough to avoid damage to the screen by overheating. At power densities in excess of 1.5 watt/cm<sup>2</sup>, the phosphor screen and the aluminum backing volatilize. Each phosphor was tested in at least two tubes. The reproducibility of the data was within the limits of  $\pm 10$  per cent.

Changes in luminescent efficiency were determined with a photocell having S4 spectral response. The spectral distribution of the fluorescence has been determined for the aged and unaged phosphors to ensure that no changes occurred which would influence the results.

#### 2.4 Other Characteristics

The temperature dependence of the luminescent efficiencies was determined in the demountable tube. The phosphors were deposited on a nickel strip which could be heated directly by passing a current through it. The same arrangement was used for determining the temperature dependence of the decay time.

The dependence of the decay time and luminescent efficiency upon exciting current density was measured in sealed-off tubes as well as in the demountable cathode-ray tube.

Particle size distributions were determined with a Sharpless Micromerograph.

Spectral distributions were measured with a Bausch and Lomb Monochromator "Model 250 mm" and a photomultiplier tube with an S11 cathode. An absolute calibration of the ensemble was made.

### III. RESULTS

There is only a limited number of phosphor types with decay times of one microsecond or less and which have at the same time properties suitable for their incorporation into a vacuum tube. They are listed in Table I, where organic materials and inorganic ones with vapor pressures too high to be used in cathode-ray tubes were not included.

Some of the general characteristics of these materials are given in publications<sup>11</sup> and a handbook edited by the various manufacturers.<sup>12</sup>

TABLE I — PHOSPHORS WITH DECAY TIMES OF 1  $\mu$ SEC OR LESS, SUITABLE FOR INCORPORATION IN VACUUM TUBES

Phosphor Type	Activator	Designation	Main Use
$(\text{CaO})_2 \cdot \text{MgO} \cdot (\text{SiO}_2)_2$	Ce	P16	TV Scanner
$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_2$	Ce	P16	TV Scanner
ZnO	Zn	P15, P24	Color TV Scanner
ZnS	Ag, Ni		Color TV
$\text{BaSO}_4$	Pb		X-Ray Screens

The present work includes all samples which were available at the time of the survey. Such a detailed study is valuable, since the characteristics of phosphors presented under one designation may vary considerably from batch to batch and from manufacturer to manufacturer.

For comparison and control of the measuring equipment some measurements on  $\text{CaWO}_4$  (P5), a cathode-ray tube and X-ray screen phosphor having relatively well known properties, were included also.

The phosphor samples were obtained from the following manufacturers: RCA, Sylvania, GE, Du Pont, US Radium Corporation, Levy and West, Derby, EMI, Leuchtstoffwerke Heidelberg, Auer, Osram, and Philips. Data on a series of ZnO phosphors prepared by the author<sup>13</sup> are also presented.

### 3.1 Light Output vs Screen Weight

The light output of a screen, observed from the face-plate side of the phosphor, goes through a maximum and then falls to zero as the screen thickness or weight is increased from zero to infinity (Fig. 2). The shape of the light output vs screen weight curve and the position of the maximum depend primarily on the scattering and reabsorption of the fluorescent light in the screen layer. It is also a function of the penetration depth of the bombarding electrons. The problem has been treated theoretically by Hamaker.<sup>14</sup>

For phosphors with a single emission band, the maximum light output is obtained when the faceplate is just fully covered with phosphor crystals and no gaps exist between the grains so that no part of the electron beam can hit the glass directly.<sup>15</sup> Complete coverage is obtained with about one to two layers of particles, depending on the particle size distribution, which in turn determines the filling factor of the layer. If the phosphor powder contains only small particles of uniform size, the coverage and consequently the light output will vary rapidly as a function of the screen weight, first increasing steeply, passing through a

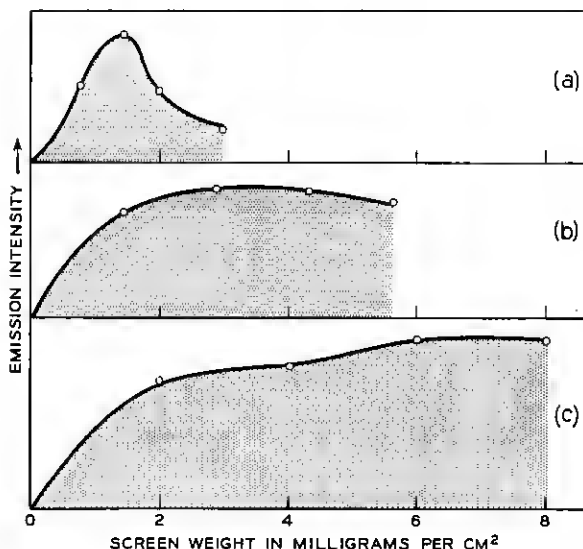


Fig. 2 — Luminescent intensity versus screen weight for three representative phosphors: (a) P16 sample #1, (b) P16 sample #2, (c) P15. Samples used for obtaining curves (a) and (b) have different particle size as shown in Fig. 3.

maximum, and decreasing rapidly. For a phosphor with a broader particle size distribution, the dependence of the light output upon the screen weight will become less critical. The relations are illustrated by Figs. 2 and 3. Phosphor sample #1 of Fig. 3 was used to obtain data of Fig. 2(a) and sample #2 for Fig. 2(b).

The phosphor shown in Fig. 2(c), a ZnO(Zn)-P15 type, is representative of a phosphor with two emission bands (blue and green for the case of P15). It is believed that the unusual form of the curve is caused by the strong reabsorption of the edge emission band, which enhances the green emission band. The phosphor therefore has a normal intensity increase with increasing screen weight up to the point of complete coverage. With further increase in screen weight, the light output increases further until the screen thickness is great enough to absorb the blue light completely. For still greater screen thicknesses the light output then decreases normally.

Table II gives a few representative values of optimum screen weight for maximum light output at 10 kv.

There is clearly a wide variation of optimum screen weights for these phosphors, all of which are designated P16, which is believed to be due

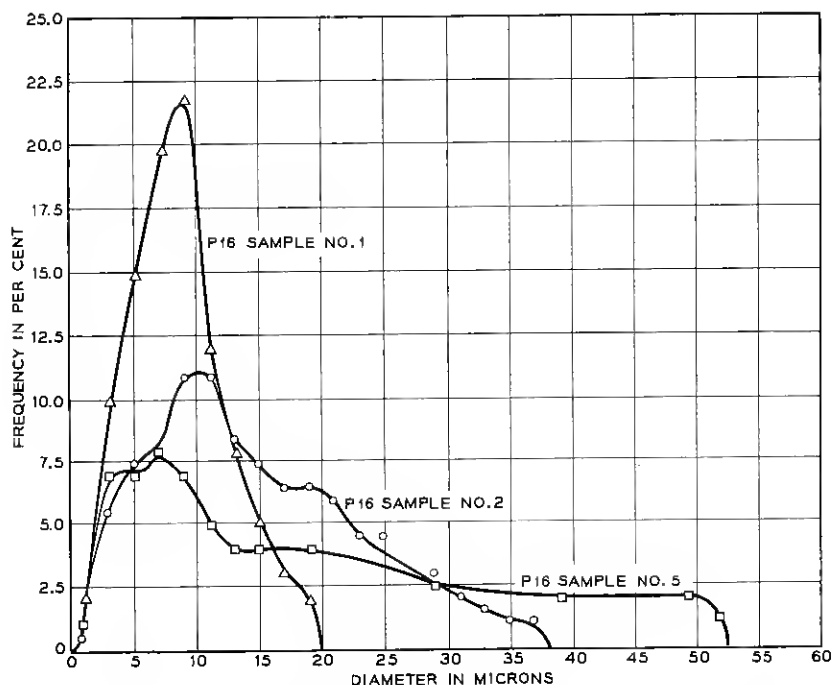


Fig. 3 — Particle size distribution of three representative P16 phosphors.

mainly to differences in particle size distribution. If reproducibility of screen performance is desired (during the settling of the final screens), care must be taken to control the particle size distribution because resolution and aging characteristics, as well as optimum screen weight, depend on it. If, for example, the average particle size is reduced by

TABLE II — MAXIMUM LIGHT OUTPUT FOR SCREENS POURED IMMEDIATELY AFTER AGITATION OF THE SUSPENSION.  
ALL P16 SAMPLES

Sample #	Composition	Maximum Intensity in Rel. Units	Optimum Screen Weight in mg/cm <sup>2</sup>
1	CaMgSilicate	100 (sharp max.)	1.5
2	CaMgSilicate	100 (flat max.)	2.8-4.2
3	CaMgSilicate	74	1.6
4	CaMgSilicate	90	2.8
5	CaAlSilicate	31	4.2
6	CaMgSilicate	103	1.4
7	CaAlSilicate (?)	49	4.2
8	CaMgSilicate	43	1.5



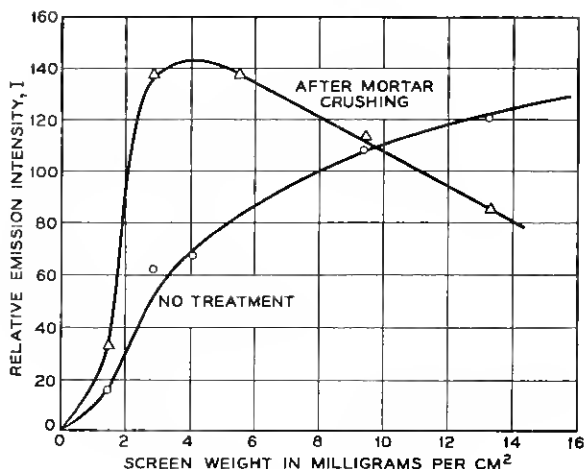


Fig. 4 — Effect of mechanical treatment of a P24 phosphor on its emission intensity and optimum screen weight.

permitting the larger particles to settle out of the suspension for a few seconds or minutes (presettling) before pouring the screen, the optimum screen weight will be less.

Heavy grinding of the phosphor should be avoided, whenever possible, as it may lead to mechanical deformations in the crystal structure and a consequent decrease in the emission intensity.<sup>15</sup> Gentle grinding may sometimes improve the screen characteristics as shown in Fig. 4. Here a P24 type phosphor with many large particles was gently crushed in a mortar. It is evident that the maximum intensity has not been changed by this treatment, but that the screen weight necessary to reach the maximum intensity was greatly reduced.

It is concluded from these data that it is necessary to determine the optimum screen weight for every settling process and every batch of phosphor, to ensure that optimum conditions are always maintained.

The particle size distribution and screen thickness could also affect the amount of light scatter within the phosphor screen and hence influence the screen resolution. Very few systematic investigations of the screen resolution could be found in the literature, but to a first approximation it has been established that the resolution is degraded in proportion to the screen thickness and is independent of the particle size (as long as the latter is small compared with the screen thickness). The reason for this behavior is that, for increasing screen thickness, the light is scattered more frequently. Table III gives some values for the resolution of cathode-ray and X-ray screens found in the literature.

TABLE III — RESOLUTION OF CATHODE-RAY AND X-RAY SCREENS

Screen Type	Screen Thickness in $\mu$	Particle Size in $\mu$	Resolution in $\mu$	Ref. No.
CR	10	10	1-6	(35)
CR	35 (estimated)	<10	52	(36)
CR	35 (estimated)	<30	49	(36)
CR	50	unknown	70	(37)
X-Ray	300	unknown	500	(38)

### 3.2 Emission Intensity and Decay Time for Unaged Phosphors

In Fig. 5, the luminescent intensity of the screen element is shown schematically as a function of time. The rise and decay follow an exponential law if the electronic process is confined to a luminescent atom, ion, or molecule, depending only on the transition probability of the luminescent transition in the center. If the luminescence is the result of the recombination of electrons in the conduction band with ionized centers, the rise and decay curves follow a second-order (bimolecular) law, with perturbations if traps are present.

The rise time will in general depend on the exciting current density. This results from the fact that an equilibrium value between the exciting and emitting processes must be reached after the beginning of the excitation and that the transition probabilities for the excitation are in general independent of those of the emission.

Under the present experimental conditions and for the phosphors studied, it was found that the rise time was always short relative to the 5-microsecond exciting pulse length, and no systematic measurements of this parameter were therefore made.

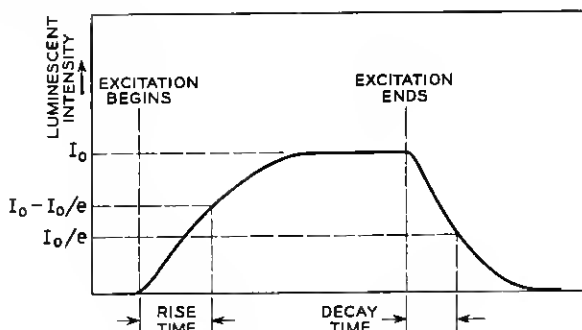


Fig. 5 — Luminescent intensity of a screen element as a function of the excitation time.

TABLE IV — EMISSION INTENSITY,  $I$ , AND DECAY TIME,  $\tau$  ( $1/e$  POINT), FOR UNAGED SAMPLES OF FAST-DECAY PHOSPHORS. 10 KV, 5 MA/CM<sup>2</sup>, PULSE LENGTH 5  $\mu$ SEC, REPETITION FREQUENCY 1000 TIMES PER SEC

Phosphor Type	Sample #	Rel. Emission Intensity	Decay Time in $\mu$ sec
P16 (CaO) <sub>2</sub> ·MgO·(SiO <sub>2</sub> ) <sub>2</sub> Ce-activated	1 (Ref.)	100	0.20
	2	100	0.25
	3	74	0.25
	4	90	0.25
	6	103	0.20
	8	43	0.30
P16 CaO·Al <sub>2</sub> O <sub>3</sub> ·(SiO <sub>2</sub> ) <sub>2</sub> Ce-activated	5	31	0.10
	7	49	0.15
P15 ZnO	1	110	1.1
	2	100	0.9
	3	81	0.75
P24 ZnO(Zn)	1	101	1.1
	2	105	0.9
	3	123	1.0
	4	85	0.45
	5	98	0.95
	6	30	0.25
	7	60	0.40
	8	88	0.75
	9	40	0.45
	10	85	0.70
	11	76	0.75
	12	55	0.45
ZnO(Zn) Laboratory Preparations	1	80	0.60
	2	71	0.55
	3	65	0.35
	4	36	0.20
	5	31	0.15
ZnS(Ag,Ni) BaPbSO <sub>4</sub>		50	0.15
		65	0.50
CaWO <sub>4</sub>	Control	50	7.5

Table IV lists the data obtained on the emission intensity,  $I$ , and decay time,  $\tau$ , of the unaged samples from various sources. The intensity values are those for optimum screen weight. Some of these data are included in Fig. 6, where the decay time is plotted as a function of the absolute intensity. For the phosphors of the P16 and P24 groups, there is clearly a strong relation between these two parameters, which can be expressed to a first approximation in the form  $I = k\tau$  ( $k = \text{constant}$ ). A similar behavior can be expected for ZnS(Ag,Ni), but a complete

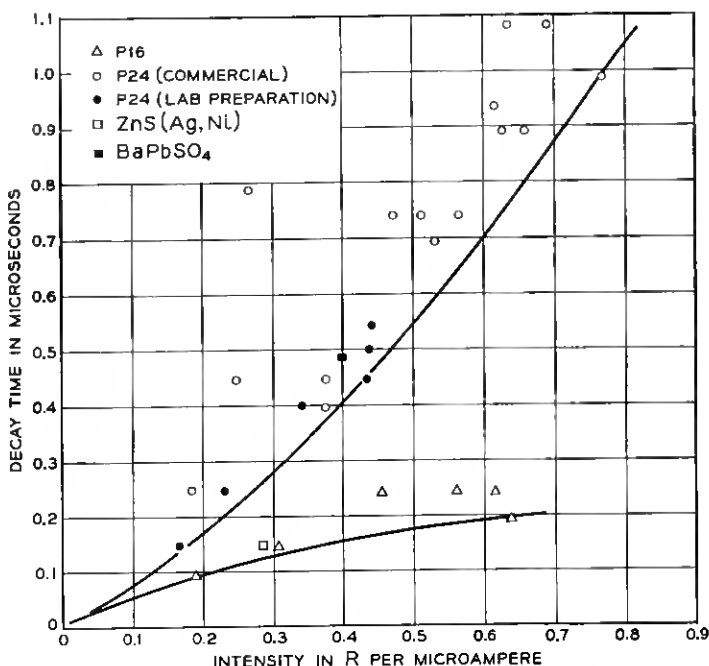


Fig. 6 — Intensity versus decay time for unaged fast-decay phosphors. One R corresponds to a light flux of  $1.1 \times 10^{-3}$  watts from a phosphor screen with P16 spectral distribution.

investigation was not possible because of the limited availability of samples. Further work on ZnO(Zn) phosphors prepared in the laboratory showed that below an upper limit, which under the given excitation conditions is of the order of 1 microsecond, any desired  $\tau$  value can be obtained by using appropriate preparation conditions.<sup>13</sup>

The proportionality between  $I$  and  $\tau$  for ZnO(Zn) is believed to be due to the fact that crystals with shorter decay time have a greater number of lattice defects introduced by firing at higher temperatures.<sup>13</sup> Radiationless transitions are induced by these defects and compete with the luminescent transitions in the excess Zn ions. Quenching effects can also be obtained by the introduction of special impurities, the so-called "killers," such as Ni, Co, or Fe in ZnS.<sup>16</sup> Quantities as low as  $2 \times 10^{-5}$  per cent of Ni in ZnS(Cu) are sufficient to have an appreciable action on deep-lying traps, thereby quenching the long-lasting afterglow without materially affecting the luminescence efficiency during excitation.<sup>17</sup> A reduction of the emission intensity at a higher Ni concentration appears with complete extinction at  $10^{-2}$  per cent Ni. The

ZnS(Ag,Ni) sample studied here is representative of the application of this quenching principle to obtain an appropriate combination of decay time and intensity.

### 3.3 Aging of Efficiency and Decay Time

Data on the changes of efficiency and decay time (aging) under electron bombardment are especially important, as published data on quantitative measurements are very limited.

The aging of the luminescence efficiency is shown in Fig. 7 for several examples of P16 phosphors, in Fig. 8 for one sample each of ZnO(Zn), ZnS(Ag,Ni), and BaPbSO<sub>4</sub>. Differences appear in the aging behavior of the P16 samples. This is due to differences in the manufacturing processes of samples of similar chemical composition as well as to the fact that some of the samples (#1, #2, #4, and #6) are of the (CaO)<sub>2</sub>·MgO·(SiO<sub>2</sub>)<sub>2</sub> type, and others (#5 and #7), of lower initial intensity, are of the CaO·Al<sub>2</sub>O<sub>3</sub>·(SiO<sub>2</sub>)<sub>2</sub> variety. All P16 samples, especially those of the Mg-silicate type, are characterized by a sharp percentage decrease of the intensity during the first 0.1 coulomb/cm<sup>2</sup>. This is not too apparent when plotted on a logarithmic scale, but the rapid initial intensity decrease makes screen preaging useful where a high degree of screen uniformity is needed.

For two P16 samples (#1 and #5), the aging of the efficiency was also determined at a lower beam acceleration voltage of 7.5 kv, and no

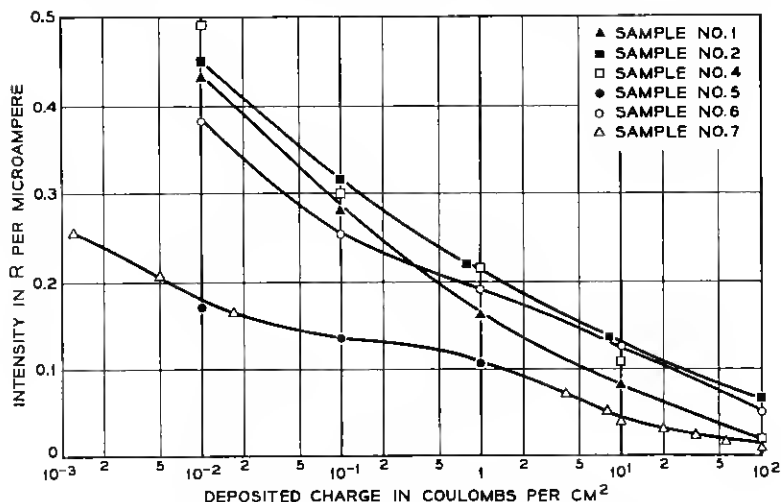


Fig. 7 — Aging of emission intensity of various P16 samples.

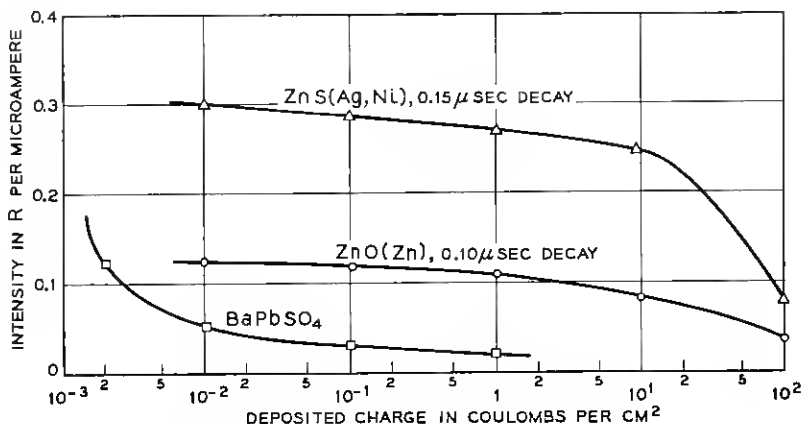


Fig. 8 — Aging of emission intensity of ZnO(Zn), BaPbSO<sub>4</sub>, and ZnS(Ag, Ni) phosphors.

difference of the aging curve as compared to 10 kv was found. Also, even though the range from 7.5 to 10.0 kv is small, it confirms previous evidence of the independence of the aging with accelerating voltage.<sup>18</sup>

Some variations were found in the aging behavior of ZnO(Zn) = P24 samples. Phosphors prepared at firing temperatures over 1000°C aged slightly faster than those prepared below this temperature.<sup>13</sup> The differences are not great enough to be of importance for the present evaluations. Otherwise, the form of the normalized aging curve remains the same, regardless of the initial intensity of the P24 sample.

Rapid aging occurs at the beginning of the bombardment for Ba·PbSO<sub>4</sub>, similar to P16. The ZnS sample, on the other hand, ages more slowly, approximating the P24 type phosphors.

In the case of Ce-activated P16, it was proposed<sup>19</sup> that the electron bombardment might act as a reducing agent, transforming the luminescent Ce<sup>3+</sup> form of the activator to the nonluminescent Ce<sup>2+</sup>. As a consequence, it was proposed to compensate for this reducing action by introduction of an oxidizer into the screen of the cathode-ray tube.<sup>20</sup> Experiments by R. C. Miller<sup>21</sup> and the author on several P16 samples were unsuccessful in achieving the desired result.

No difference in the aging curves for a P16 and a P24 sample was found between pulsed or direct current excitation. The result is important as it shows that accelerated aging tests can be performed with validity, at least within reasonable limits.

The aging data given in this survey are valid only to the first approximation, as phosphors with the same chemical composition and the

same activators may show variations in behavior depending both upon differences in physical characteristics of the material and operating conditions. Particle size, form of crystallization, operating temperature, vacuum, and mode of excitation are all important parameters that must be known and maintained under control.

The decay time of all phosphors studied decreased with increasing electron bombardment. The greatest change occurred with P16 type samples (CaAl-silicates) for which a deposit of 0.04 coulombs/cm<sup>2</sup> reduced the decay time from about 200 nsec to 50 nsec or less. After this initial decrease, further reduction of  $\tau$  was small. The decay time of the P24 type phosphors decreased by about 20 per cent after 40 coulombs/cm<sup>2</sup>, independent of the initial value. Similar behavior was found for aging of ZnS(Ag,Ni) and BaPbSO<sub>4</sub>.

The principal aspects of aging behavior under electron bombardment can be summarized as follows: The aging data can be represented, to a first approximation, by the formula  $I = I_0/(1 + CN)$ , where  $I_0$  = initial intensity,  $I$  = aged intensity,  $C$  = burn parameter (a constant for a given phosphor), and  $N$  = number of electrons deposited per cm<sup>2</sup>.<sup>22,23</sup> Phosphors with larger particles age more slowly than those with smaller particles.<sup>24</sup> The form of crystallization has some influence on the aging, with phosphors quenched from higher firing temperatures aging faster in general.<sup>25,26</sup> Aging rates increase at higher sample temperatures, but the acceleration voltage has practically no influence.<sup>18</sup>

The mechanism of the aging process depends on the specific material and the type of exciting radiation. In general, there are two possibilities: (a) the bombardment destroys the luminescent center, e.g., changes the valence of the activator ion, or (b) it introduces defects which act as recombination centers for radiationless transitions.<sup>27,28</sup> The first process probably applies to all materials where the luminescent process takes place in one ion or group of ions, such as organic molecules, CaWO<sub>4</sub>, etc. Phosphors with second-order kinetics, such as ZnS, ZnO, etc., are probably in the second group. If the phosphor is exposed to exciting radiation in an atmosphere which reacts with the material, further changes may take place. A well known phenomenon illustrating this effect is the photolysis of ZnS.<sup>29</sup>

### 3.4 Other Important Parameters

#### 3.4.1 Form of Decay

Fig. 9 shows the decay curves (form of the decay) of the various phosphors studied. None of them showed an exponential decay, except

$\text{CaWO}_4$ , which previously has been measured<sup>30</sup> and is shown here only for comparison. As would be expected for phosphors with recombination type of luminescence, at least a portion of the decay is due to the presence of traps. This explains the long tail of the afterglow at low levels of intensity.<sup>31</sup> In  $\text{ZnO}(\text{Zn})$  the presence of traps was shown by glow curves<sup>32</sup> and conductivity measurements.<sup>33</sup>

During the excitation and at the beginning of the decay, the concentration of excited electrons and ionized centers is large. Thus, the rate of the second-order processes, e.g. transition of electrons from the conduction band to the excited or upper state of the center, can become larger than the transition within the center which is responsible for the luminescence. Consequently an exponential decay could be observed initially with a decay constant characteristic for the transition within the center (activator). This effect is clearly present at the beginning of the decay of P16 and  $\text{BaPbSO}_4$  phosphors (Fig. 9).

The increase in the recombination rate with increasing excitation density results in a decrease of the decay time. Fig. 10 shows this effect for P16 and P24 phosphors. Similar behavior was found for  $\text{BaPbSO}_4$  and  $\text{ZnS}(\text{Ag}, \text{Ni})$ .

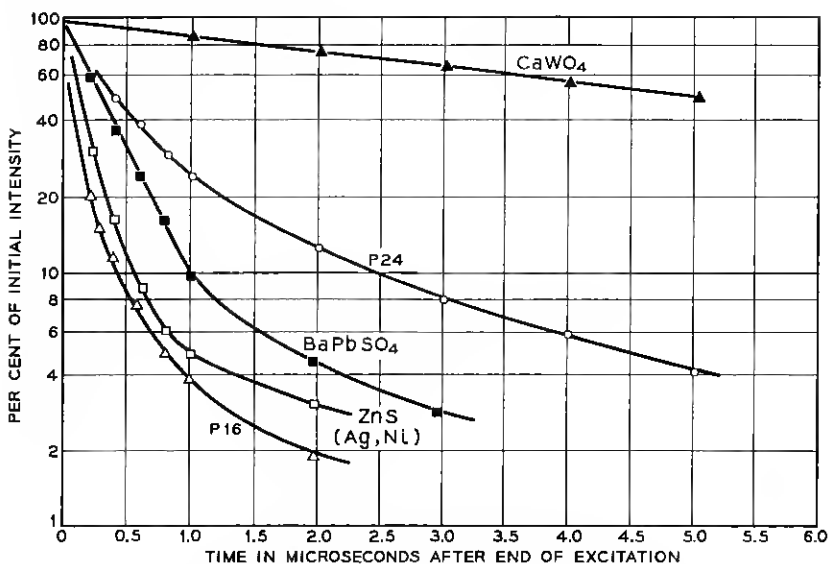


Fig. 9 — Form of decay of various fast-decay phosphors.



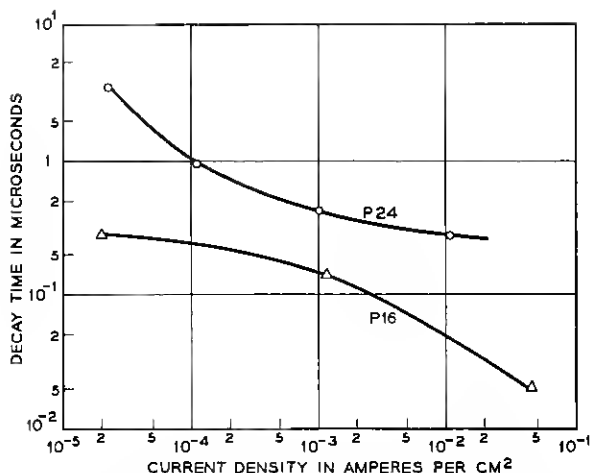


Fig. 10 — Decay time of a representative P16 and P24 sample as a function of the excitation level (as determined by the exciting current density).

### 3.4.2 Temperature Dependence of Intensity and Decay Time

An increase in temperature enhances, in general, the probability of radiationless transitions and should therefore result in a reduction of  $I$  and  $\tau$ . This is shown in Figs. 11 and 12 for the fast-decay phosphor types studied here.  $\text{ZnO}(\text{Zn})$ ,  $\text{ZnS}(\text{Ag}, \text{Ni})$ , and  $\text{BaPbSO}_4$  exhibit a decrease of both parameters with increasing temperature. P16 is an exception, as its intensity increases slightly above room temperature and decreases for temperatures exceeding  $150^\circ\text{C}$  and  $400^\circ\text{C}$  for the aluminum and magnesium silicates respectively. This is similar to the behavior of Mn-activated silicate phosphors<sup>34</sup> which are frequently preferred for projection kinescopes despite a lower intensity at room temperature as compared with  $\text{ZnS}$ -type phosphors.

### 3.4.3 Spectra

The spectra of the various fast-decay phosphors are shown in Fig. 13. No variation of the spectral distribution was observed during the aging for any of the fast-decay samples.

## IV. CONCLUDING REMARKS

The data obtained in this study show that phosphors obtained under one designation and of the same chemical composition show wide varia-

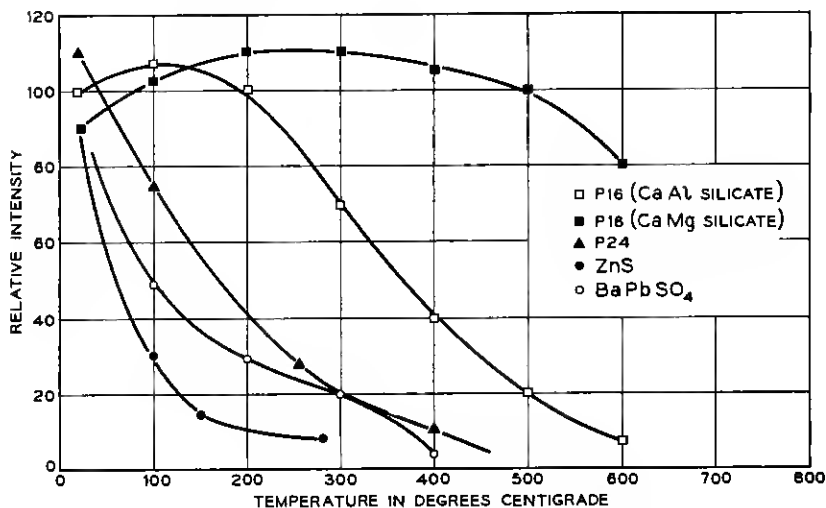


Fig. 11 — Temperature dependence of emission intensity for various fast-decay phosphors.

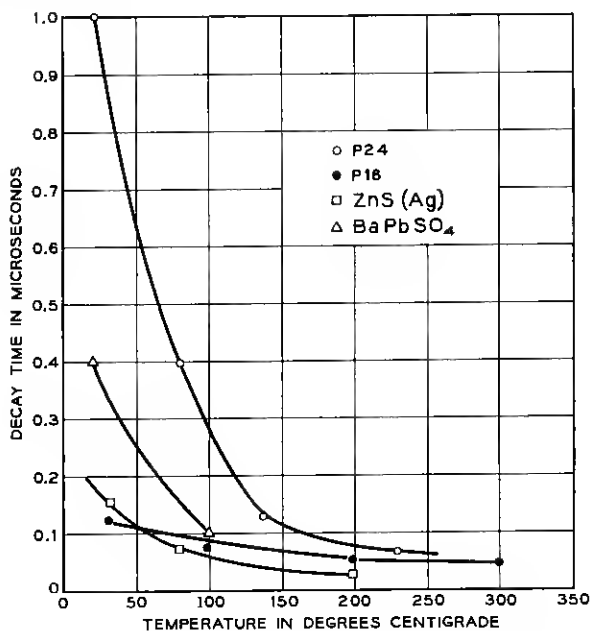


Fig. 12 — Temperature dependence of the decay time of fast-decay phosphors.

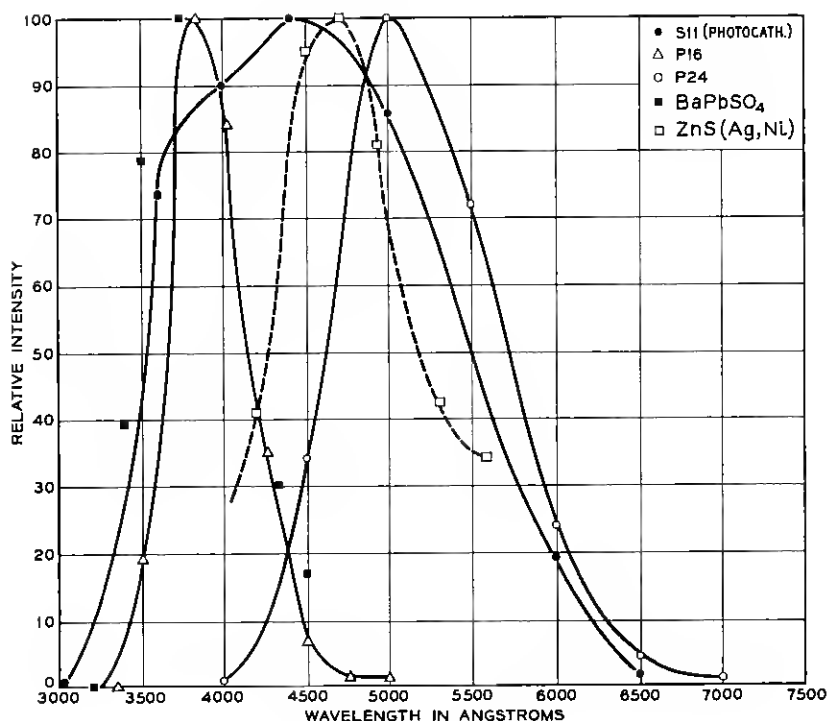


Fig. 13 — Distribution of the spectral emission of various fast-decay phosphors.

tions of their properties. This, of course, is to be expected as the luminescent properties depend on the incorporation of small amounts of activators as well as on crystal defects which might be introduced during the preparation.

Several samples of a given phosphor must therefore be evaluated to obtain the range of variations of its intensity, decay time, and optimum screen weight. In this manner the optimum phosphor can be selected for a specific application. Such a survey will be especially necessary if the screen performance is near the limit of the system requirements.

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